

CONSIDERATIONS ON BIMETALLIC INTERMEDIATES IN METATHESIS

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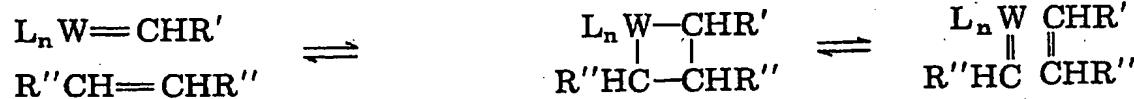
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Summary

The activity of the catalyst system $\text{WOCl}_4/\text{Me}_4\text{Sn}$ in metathesis was found to depend on the presence of the co-catalyst derivative Me_3SnCl . Me_3SnCl is essential to maintain the activity of this catalyst, and on complete removal of Me_3SnCl , the catalyst becomes inactive. This is inconsistent with the simple carbene mechanism which is generally accepted for metathesis reactions, as no role of the co-catalyst (derivative) in the active species is included. To date, arguments in favour of this chain mechanism are provided by studies merely regarding the initiation and propagation of the reaction. A more comprehensive mechanism is presented which involves initiation, propagation, and termination also. This scheme is governed by Lewis acids, i.e. co-catalyst derivatives. The suggested intermediates are bimetallic alkylidene bridged complexes.

Introduction

The metathesis reaction has drawn extensive attention not only for its synthetic importance, but also because its mechanism has intrigued many workers [1 - 4]. So far, a number of reaction mechanisms has been suggested. In the literature, there is a growing consensus that metallocarbene and metallocyclobutane complexes are key components in metathesis [5]. This so-called carbene mechanism is thought to proceed as follows:



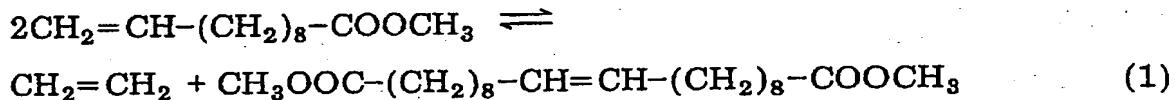
This concept is mainly supported by (i) kinetic studies, (ii) the metathesis related chemistry of isolable tungsten carbene complexes, and (iii) studies concerning the first-formed products. In these studies only the initiation and the propagation steps of the chain reaction scheme are considered.

In bicomponent catalyst systems, the initial metallocarbene species are generated by reaction of non-carbenoid species, *i.e.* catalyst and co-catalyst. Subsequently, the transition metal of the catalyst acts as an alkylidene carrying and transferring centre. The co-catalyst derivative is not part of the active intermediates. A possible interaction between the active intermediate and co-catalyst derivatives has already been suggested, though no experimental evidence was provided [6].

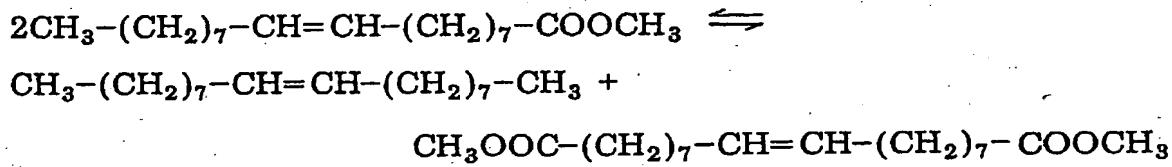
We have investigated the metathesis of methyl 10-undecenoate and of methyl oleate by the catalyst system $\text{WOCl}_4/\text{Me}_4\text{Sn}$ and have found that the presence of the co-catalyst derivative Me_3SnCl is essential to maintain the activity of this catalyst system. These findings are inconsistent with the above scheme. Therefore, I wish to present here a more comprehensive reaction scheme involving initiation, propagation, and termination also, governed by co-catalyst derivatives. This scheme is partially based on experimental data presented below and partially on results reported in literature.

Results

Metathesis reactions are thermoneutral in the case of simple olefins [4]. Consequently, metathesis reactions are, in general, not completed in one way or another. This also holds for the metathesis of long-chain unsaturated acid esters [7]. In an attempt to increase the yield of the metathesis reaction of methyl 10-undecenoate (eqn. (1)) we intended to remove the produced ethene by evacuation of the reaction vessel.



The reactions were carried out by using $\text{WOCl}_4/\text{Me}_4\text{Sn}$ as a catalyst (molar ratio: ester/W/Sn = 50/1/1; $T = 343\text{ K}$). For comparison, the reaction was first allowed to proceed in a closed reaction vessel. The course of the reaction was similar to that of unsaturated acid esters which does not produce volatile reaction products, *e.g.* methyl oleate (see Fig. 1):



As ethene partially escapes into the gaseous phase enclosed in the reaction vessel, the ultimate conversion in the metathesis of methyl 10-undecenoate amounted to approximately 60%. Subsequently, a series of experiments was carried out in which ethene was removed in different ways:

— In an experiment, the reaction vessel was continuously evacuated after 1 h. In this way, not only was the ethene produced vented, but also the relatively volatile co-catalyst derivative Me_3SnCl (1). In the off-gas, the pres-

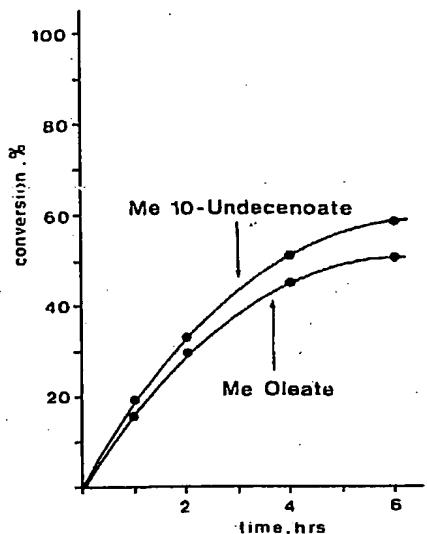


Fig. 1. Comparison between the metathesis of methyl oleate and of methyl 10-undecenoate by $\text{WOCl}_4/\text{Me}_4\text{Sn}$ (molar ratio: ester/W/Sn = 50/1/1; $T = 343 \text{ K}$).

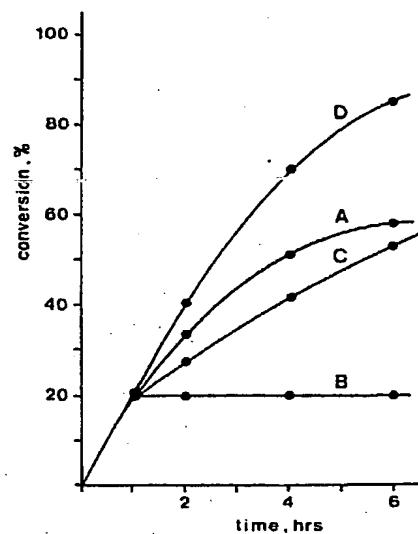


Fig. 2. Metathesis of methyl 10-undecenoate by $\text{WOCl}_4/\text{Me}_4\text{Sn}$ (molar ratio: ester/W/Sn = 50/1/1; $T = 343 \text{ K}$). Closed reaction vessel (A); closed reaction vessel, 95% of Me_3SnCl removed by continuous evacuation after 1 h (B); closed reaction vessel, 42% of Me_3SnCl removed by evacuation during 5 min after 1 h (C); reaction vessel with a small leak, < 5% of Me_3SnCl escaped (D).

ence of methane, ethene, and 1 and traces of ethane, HCl , and methylchloride was established. These are common products of catalyst activation [6, 8]. No other products were found. Based on the assumption that Me_4Sn is completely converted into 1 during activation, it was found that 95% of 1 was removed from the reaction vessel within 15 min. This resulted in complete deactivation of the catalyst and the reaction stopped (Fig. 2, curve B).

— If only part of 1 was removed (approximately 42%) a considerable decrease in activity was observed (Fig. 2, curve C). Partial removal of the product 1 was achieved by evacuation of the reaction vessel for 5 min after 1 h. As the ethene produced within 1 h was also removed, the ultimate conversion was higher than that in a closed reaction vessel.

— In experiments conducted under constant pressure, the conversion steadily increased until almost completion of the reaction (Fig. 2, curve D). In this case the ethene produced was vented by a small leakage in the reaction vessel. Only a small amount of 1 could escape (*i.e.* < 5%).

These results suggest that the co-catalyst or its derivatives are essential for the activity of the employed catalyst. However, it may not be excluded that an unknown termination reaction is induced by evacuation. Therefore, control experiments were performed in which the reaction was allowed to proceed in a closed reaction vessel under vacuum. This was achieved by evacuation of the closed reaction vessel before activation with Me_4Sn . Then, Me_4Sn was added by syringe, so that the vacuum was maintained during the

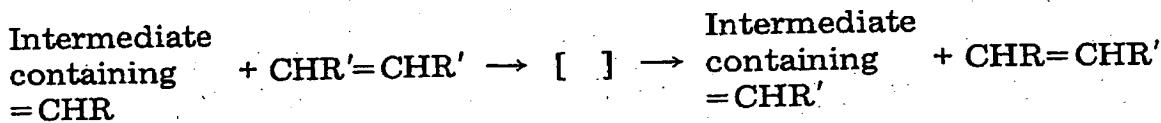
reaction. In these cases the reaction proceeded similar to that in a closed vessel under ambient pressure (Fig. 2, curve A).

In metathesis reactions of methyl oleate, a similar dependence was found for the observed activity and the amount of 1 removed. It has not yet precisely been established to what extent the presence or the absence of 1 determines the activity of the catalyst. This is due to the moderate reproducibility of the activity of the catalyst caused by contaminates such as water and oxygen which are introduced by taking samples by syringe. Yet, in all cases, removal of 1 resulted in a decreased activity which could not be restored by stopping evacuation nor by the addition of fresh 1 or other products of catalyst activation. Addition of fresh Me_4Sn also hardly affected the reduced activity.

Discussion

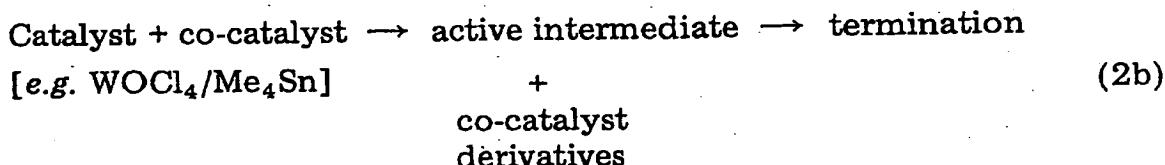
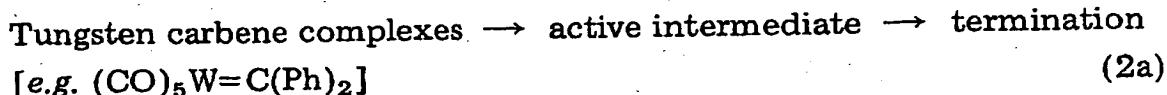
From the above results, it can be concluded that the presence or the absence of the co-catalyst derivative 1 is essential to maintain the activity of the catalyst system $\text{WOCl}_4/\text{Me}_4\text{Sn}$. These findings are inconsistent with a simple carbene mechanism. Therefore, the arguments in favour of this mechanism have to be reconsidered.

On closer examination, the evidence based on kinetic studies [9 - 13] and on studies concerning the first-formed products [14 - 18] only points to intermediates which contain at least one alkylidene moiety and which are able to exchange one of these alkylidene moieties with an alkene at the time:



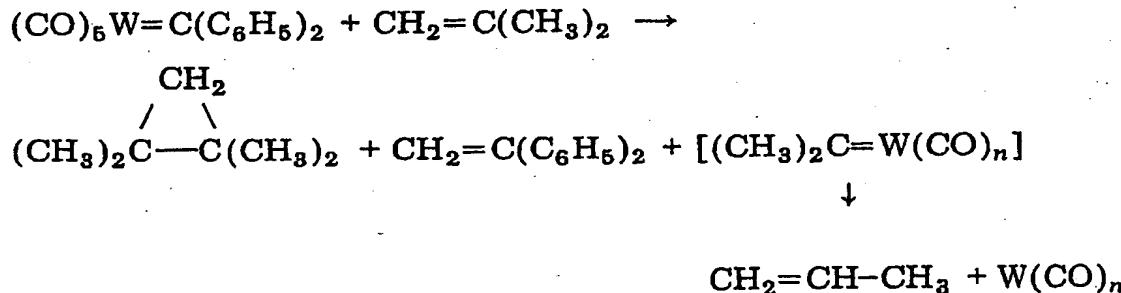
This includes simple carbene complexes. However, other and/or more complex intermediates are not excluded.

With regard to isolable tungsten carbene complexes, there are obvious discrepancies in chemical behaviour between these complexes and metathesis catalysts under usual reaction conditions. The ineffectiveness and the sensitivity for terminating side-reaction of these complexes is particularly striking, as the only difference is the presence or the absence of co-catalyst derivatives:



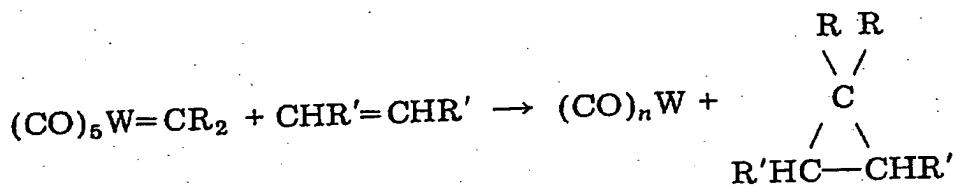
An example of the ineffectiveness of tungsten carbene complexes in metathesis is the activity of $(CO)_5W=C(Ph)_2$. After 40 h, only a 44% conversion of (Z)-2-pentene is achieved (molar ratio: alkene/W = 80 - 100/1; $T = 298\text{ K}$) [18]. No catalytic activity remained after such a long period of time. In comparison, systems such as $W(CO)_5L/EtAlCl_2/O_2$ ($L = CO, P(Ph)_3, P(OPh)_3$) convert 2-pentene within 25 min into an equilibrium mixture of 2-butene and 3-hexene, i.e. 52% conversion (alkene/W molar ratio: 100/1; $T = 298\text{ K}$) [19]. According to the carbene mechanism, this can only be explained by the stability of isolable tungsten carbene complexes used as a catalyst precursor. Firstly, one alkylidene interchange has to take place leading to an unstable and reactive complex (eqn. (2a)). Then this newly formed carbene complex can metathesize the remaining alkene molecules. Consequently, the reaction rate would be very limited at the beginning and steadily increase in the course of the reaction. Such data have not been reported. As an equilibrium between formation and disintegration of reactive species may be presumed, the lack of such data may rise from a limited steady state concentration due to the limited lifetime of such species, i.e. $\text{rate}_{\text{formation}} \leq \text{rate}_{\text{disintegration}}$ (eqn. (2a)). The apparent activity of the catalyst can be raised by increasing the rate of formation and/or by decreasing the rate of disintegration. In the former case, the apparent lifetime of the catalyst would be limited. By decreasing the rate of disintegration, a longliving catalyst is obtained with an increased activity. Apparently, this can be accomplished by stabilizing agents. It was demonstrated that the activity of tungsten carbene complexes such as $(CO)_5W=C(OMe)R$ ($R = CH_3, C_6H_5$) is strongly enhanced by Lewis acids such as $(i\text{-}Bu)_2AlH, AlCl_3$ and $Et_3Al_2Cl_3$ [20]. Although $(CO)_5W=C(OMe)Et$ treated with these organo-aluminium compounds is almost inactive in metathesis of 1-pentene (probably due to degenerate metathesis), on addition of NR_4Cl the metathesis of 1-pentene could be observed [21]. The organoaluminium compounds used in these experiments are well-known co-catalysts and/or co-catalyst derivatives in bicomponent catalysts.

The sensitivity of tungsten carbene complexes for terminating side-reactions has been demonstrated in numerous reports concerning stoichiometric reactions of these carbene complexes with alkenes [22 - 25]. For example, in the reaction of (diphenylcarbene)pentacarbonyltungsten with isobutene, the expected dimethylcarbene complex was not detected. Instead, considerable amounts of propene were produced [25]:

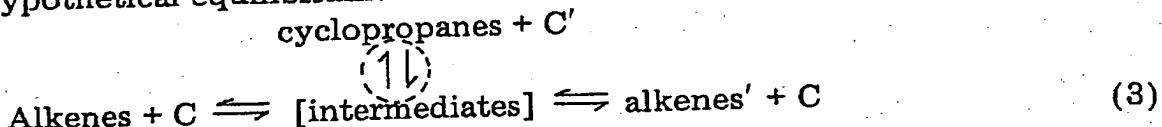


If this mode of termination would occur at such an extent in reactions with catalysts activated with alkylating agents, the catalyst would become inactive within a few turnovers.

Furthermore, tungsten carbene complexes readily react with alkenes yielding cycloalkenes:



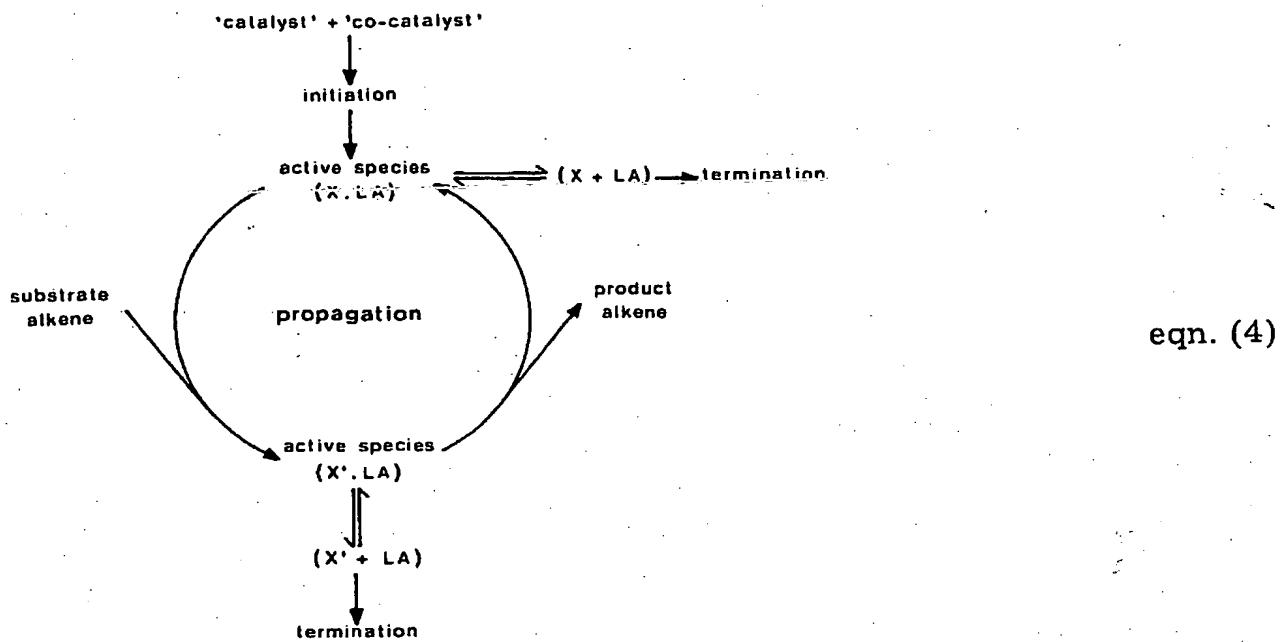
This reaction often accompanies metathesis reactions induced by isolable tungsten carbene complexes. Therefore, Mango [26] considered the following hypothetical equilibrium:



C and C' are catalytic species. From the calculated equilibrium constant of the system: ethene/cyclopropane, it was concluded that a carbene mechanism should imply the formation of cyclopropanes to some observable extent under metathesis reaction conditions. However, cyclopropanes are not generated over active catalysts. Consequently, it seems doubtful that alkene metathesis proceeds via the suggested carbene mechanism.

Again, an important aspect of the objections against the simple carbene mechanism is the instability and the ineffectiveness of the proposed intermediates. Apparently, co-catalyst derivatives are able to control these factors. Moreover, it has already been established that (i) alkyltungsten and tungsten carbene complexes strongly interact with Lewis acids, *i.e.* co-catalyst derivatives [6, 20, 21], and (ii) no soluble tungsten compounds are present in the hybrid catalyst derived from WCl_6 and Me_3Sn - anchored to a polymer [27]. Consequently, it is very likely that the involved catalytic species interact with Lewis acids resulting in, for example, bimetallic complexes.

As the catalytic species C' from eqn. (3) contain no alkylidene moiety(s), a possible interaction between C' and a Lewis acid involves a minor free energy change than the interaction between C and a Lewis acid. Hence, Lewis acids govern the reaction according to eqn. (3) by this interaction, and the formation of cyclopropanes becomes in the presence of Lewis acids less favourable. For these considerations, I suggest the following diagram for metathesis reactions induced by bicomponent catalyst systems (cf. eqn. (4)). This scheme is fully consistent with the observations mentioned above. Moreover, it can account for a number of other phenomena of the metathesis chemistry. The supposed equilibria between stabilized and non-stabilized intermediates play a major role, as a shift of these equilibria to non-stabilized species directly influences the apparent activity of the system.



The activity of $\text{WCl}_6/\text{R}_n\text{M}$ systems varies markedly with the applied co-catalyst. Its alkylating power is not the only factor which determines the resulting activity, but also the Lewis acidity of the derivatives is of great importance. For example, the moderately active system WCl_6/BuLi becomes on addition of AlCl_3 as active as the highly active system $\text{WCl}_6/\text{EtAlCl}_2$ [28]. Furthermore, the ratio W/alkene and W/solvent influences the optimal ratio catalyst/co-catalyst owing to interactions with the substrate and the solvent. This may account for the fact that distinct catalyst systems are unable to induce metathesis reactions at high alkene/W ratios, e.g. $\text{WOCl}_4/\text{Me}_4\text{Sn}$.

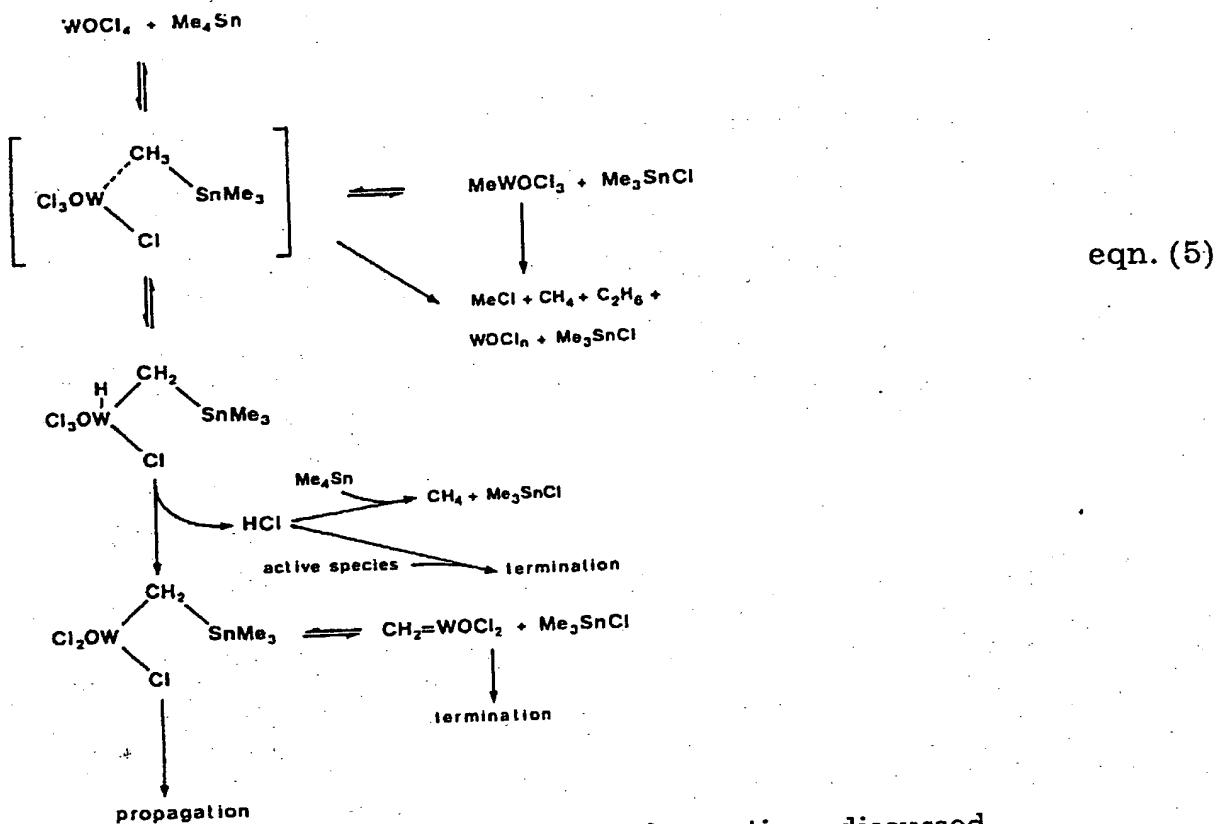
It is known that addition of Lewis bases such as pyridine and acetonitrile suppresses side-reactions if added before activation of the catalyst [29]. However, when added to an active catalyst they strongly inhibit metathesis reactions [30]. It is obvious that Lewis bases added before activation can interact with Lewis acidic species such as WCl_6 and WOCl_4 and consequently act as an additional ligand which influences the activity and selectivity. When added to the *in situ* catalyst, interaction results in destabilization of the active species and a lower activity is expected.

In some metathesis experiments, small quantities of cyclopropanes, not exceeding the amount of catalyst, were detected after quenching with a dilute HCl solution [31]. These results also can be made plausible by assuming that, on quenching, the active intermediates are destabilized and open for the same mode of termination as isolated tungsten complexes.

From the results described above, the structure of the suggested adducts remains uncertain. Yet, recent reports provide an insight into the interference of Lewis acids with carbene complexes. Electrophilic carbene complexes, which are able to induce metathesis related reactions, are unstable in the presence of Lewis acids [32]. In contrast, nucleophilic alkylidene

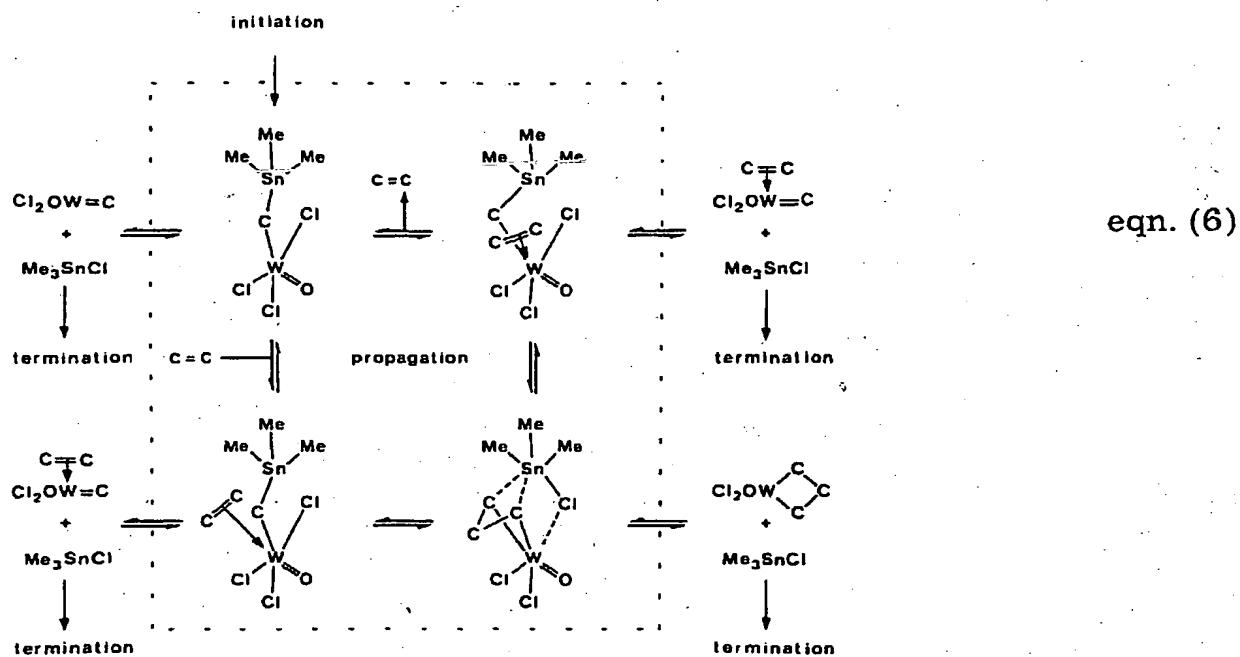
(carbene) complexes form stable adducts [33, 34]. Similar adducts of titanium with organoaluminium compounds are able to induce degenerate metathesis [35]. However, no stable alkylidene complex of tungsten has been described. As all the species involved in catalyst systems derived from WCl_6 and WOCl_4 are more or less strong Lewis acids, the interference of neutral or nucleophilic tungsten carbene complexes is very likely.

On account of these considerations, I suggest the following reaction scheme for the system $\text{WOCl}_4/\text{Me}_4\text{Sn}$:



These schemes are consistent with the observations discussed.

Objections seem only to arise from stereoselectivity studies. As demonstrated in the early stage of metathesis reactions, the (E)/(Z) ratios of the alkenes produced considerably deviate from the ratio at equilibrium; this is, in general, in accordance with thermodynamics [36 - 38]. These deviations were found to be independent of the applied co-catalyst for different tungsten catalysts. It is possible that this excludes a direct interference of Lewis acids at the active site. However, many explanations have been suggested for the observed stereoselectivities. An important aspect seems to be the preference for certain stereoalignments of alkenes to the active site. This would result in a preferential formation of (E)-products from (E)-alkenes and of (Z)-products from (Z)-alkenes. To which extent, Lewis acids may influence the stereochemistry is uncertain. Therefore, rejection of the suggested bimetallic intermediates on account of these objections seems



premature. At the same time, it indicates that more experimental data are required to provide conclusive evidence.

Experimental

Methyl oleate and methyl 10-undecenoate were purified by distillation. The distillates were dried over molecular sieves and stored under nitrogen. Tetramethyltin (Merck) was dried with molecular sieves. As catalysts, both unpurified WCl_6 and pure WOCl_4 were used. According to analysis, the composition of unpurified WCl_6 was $\text{WO}_{0.8-1.3} \text{Cl}_{4.4-8.4}$. WOCl_4 was obtained by careful sublimation of unpurified WCl_6 .

The metathesis reactions were carried out in 50-ml, two-necked, round-bottomed flasks equipped with a silicon rubber seal and connected with a vacuum-line (65 Pa) via a trap cooled with liquid nitrogen. The reaction mixtures were stirred and heated in a thermostated ultrasonic bath. The order of addition in preparation of the reaction mixtures was: ester, tungsten chloride, and tetramethyltin. In all cases the molar ratio ester/W/Sn was 50/1/1.

In a typical example, a mixture of 10 g (50.5 mmol) methyl 10-undecenoate, 340 mg (1.0 mmol) WOCl_4 , and 135 μl (1.0 mmol) Me_4Sn was prepared under nitrogen, and heated to 343 K. After 1 h, the reaction flask was evacuated for 5 min. By syringe, samples were taken just before evacuation, and after 2, 4, 6, and 18 h, GLC analysis indicated that methyl 10-undecenoate was converted 20%, 27%, 41%, 50% and 75%, respectively. In all cases a selectivity greater than 96% was observed.

GLC and mass spectrometry analysis indicated that ethene, as the main product, escaped from the reaction mixture. Besides, methane, ethane, trimethyltin chloride and traces of HCl and methylchloride were found. The products were identified by use of authentic samples. When the trap was heated to 303 K, pure Me_3SnCl remained. Therefore, it was quantitatively determined by weighing.

No differences were found between catalysts derived from unpurified WCl_6 and catalysts from WOCl_4 .

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